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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : C07D 239/42, 401/14, 213/73, C07C 311/29, A01N 47/36 — A1

(11) International Publication Number: WO 96/12708

(43) International Publication Date: 2 May 1996 (02.05.96)

(21) International Application Number: PCT/KR94/00147

(22) International Filing Date: 24 October 1994 (24.10.94)

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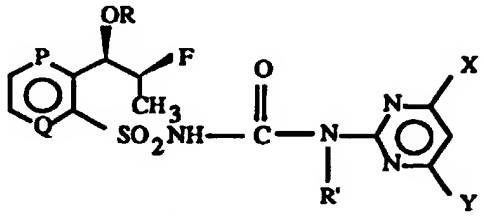
(81) Designated States: AU, CA, CN, JP, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published
With international search report.

(54) Title: HERBICIDAL SULFONYL UREA DERIVATIVES

(57) Abstract

The present invention relates to novel sulfonyl urea derivatives of formula (I) having erythro-type stereoisomer as herbicides for treatment of pre-emergence and/or post-emergence, their use and composition as agriculturally suitable herbicides, wherein, P and Q, as equivalent or different group respectively, are CH or N, and present as aromatic ring including P and Q as benzene or pyridine ring; R is H, (a) or (b) group, wherein R^a is C_1 ~C_4 alkyl, C_1 ~C_3 haloalkyl, C_2 ~C_4 alkenyl or C_2 ~C_4 alkynyl group, wherein X^a is O, S, NH or NR^a group; R' is H or CH_3 group; and X and Y are independently halogen atom, C_1 ~C_2 alkyl, C_1 ~C_2 alkoxy or C_1 ~C_2 haloalkoxy group.



(I)

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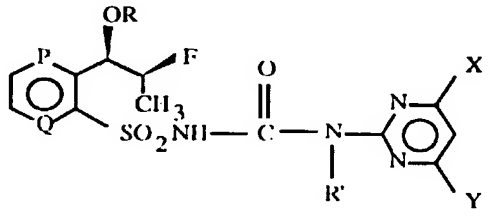
HERBICIDAL SULFONYL UREA DERIVATIVES

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to novel sulfonyl urea derivatives of the following formula (I) having erythro-type stereoisomer as herbicides for treatment of pre-emergence and/or post-emergence, their use and composition as agriculturally suitable herbicides.



(I)

wherein,

P and Q, as equivalent or different group respectively, are CH or N, and present as aromatic ring including P and Q as benzene or pyridine ring ;

R is H, $R^a-\overset{O}{\overset{\|}{C}}-$ or $R^a-X^a-\overset{O}{\overset{\|}{C}}-$ group, wherein R^a is C_1 ~C_4 alkyl, C_1 ~C_3 haloalkyl, C_2~C_4 alkenyl or C_2 ~C_4 alkynyl group, wherein X^a is O, S, NH or NR^a group;

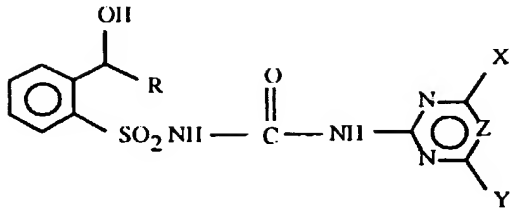
R' is H or CH_3 group; and

X and Y are independently halogen atom, C_1~C_2 alkyl, C_1~C_2 alkoxy or C_1~C_2 haloalkoxy group.

Description of the Prior Art

It is publicly well-known that sulfonyl urea derivatives possess a herbicidal activity. Such examples containing sulfonyl urea are;

(1) Korea Patent publication No. 93-9825 discloses the compound having the following formula(A)



(A)

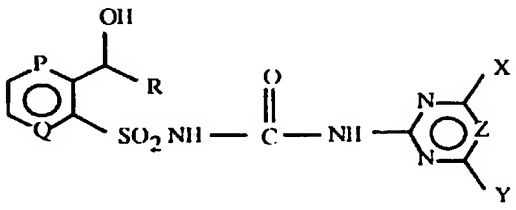
wherein,

R is haloalkyl ;

X and Y are independently CH_3, OCH_3 or Cl etc. ;

Z is CH or N.

(2) Korea Patent publication No. 93-9507 discloses the compound having the following formula(B)



(B)

wherein,

R, X, Y and Z are as previously defined,

P and Q are differently N or CH.

If R group of the above formula(A) and (B) includes asymmetric carbon atom, then the above compound has two stereoisomers which are threo- and erythro-type by reason of two asymmetric carbon atom. But herbicidal activity and selectivity of the above stereoisomers have been not disclosed.

SUMMARY OF THE INVENTION

The object of the present invention is to provide novel sulfonyl urea derivatives having very prominent herbicidal activities toward rice and wheat and also possess a good selectivity for annual and perennial weed, especially a barnyard grass.

Another object of this invention is to provide herbicidal compositons containing said derivatives as active compounds.

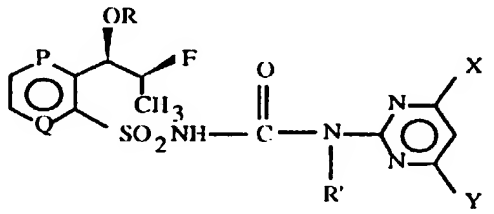
BRIEF DESCRIPTION OF THE INVENTION

Fig. 1 is stereoconfiguration based upon X-ray crystallography analysis of the compound manufactured by EXAMPLE 1.

Fig. 2 is stereoconfiguration based upon X-ray crystallography analysis of the compound manufactured by EXAMPLE 9.

DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to herbicidal sulfonyl urea derivatives with substituent of erythro-type stereoisomer having the following formula(I), which have herbicidal selectivity toward rice and wheat, and their agriculturally suitable salts.



(I)

wherein,

P, Q, R, R', X and Y are as previously defined.

A preferred group of erythro-type stereoisomer of the above formula(I), in view of a strong activity and a good selectivity is as follows :

(1) Benzene(P and Q are independently CH)

(2) Pyridine(P is N, and Q is CH)

(3) R is hydrogen atom

(4) R' is hydrogen atom

(5) R is acetyl group

(6) X and Y are methoxy group.

These compounds can easily control barnyard grass as well as a perennial weed causing trouble for rice and can be used agriculturally as herbicidal composition for rice. Especially the following compounds have a good selectivity for rice :

Erythro *N*-[(4,6-dimethoxy-pyrimidin-2-yl)aminocarbonyl]-2-(2-fluoro-1-hydroxy-n-propyl)-3-pyridinesulfonamide,

Erythro *N*-[(4,6-dimethoxy-pyrimidin-2-yl)aminocarbonyl]-2-(2-fluoro-1-hydroxy-*n*-propyl)-benzenesulfonamide, etc..

The erythro-type compounds of the above formula(I) according to the present invention have more prominent herbicidal activity than threo-type or mixture of erythro- and threo-type. Furthermore, the erythro-type compounds of the above formula(I) may be used as herbicides or active ingredient of herbicidal composition because of a good selectivity for rice and wheat.

A pure compound of erythro-type having the above formula(I) according to the present invention can be prepared by reactions described in herein below, but should not be constructed to be limited hereto.

The compound of the above formula(I), in which R is hydrogen atom, can be obtained by hydrolyzing the compound of the above formula(I), where R is acyl group such as acetyl group, in present of alkali.

In order to hydrolyze the above acyl group, alkali such as LiOH, KOH, NaOH, Li_2CO_3, Na_2CO_3, K_2CO_3, etc., preferably LiOH, may be used.

The above hydrolysis reaction is carried out under water or organic solvent, as a mixture of water with unreacting solvent such as methanol, ethanol, acetone, tetrahydrofuran, dimethylformamide, etc., or solvent alone. The hydrolysis occurs at the temperature of 0 ~ 80 ℃ in a reaction time of 1~24 hours, and then the obtained product may be easily seperated by acidifying with aqueous HCl solution.

As an other process, after acidifying, the obtained product is extracted with methylene chloride, ethyl acetate, etc. and then concentrated to obtain the final product. If necessary, a pure product can be obtained by purification using HPLC.

The hydrolysis in the above reaction is carried out as shown in the following reaction scheme.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR00/01138

A. CLASSIFICATION OF SUBJECT MATTER

IPC7 C07D 401/12, C07D 213/26, A01N 43/40

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimun documentation searched (classification system followed by classification symbols)
IPC 7 C07D

Documentation searched other than minimun documentation to the extent that such documents are included in the fileds searched
Korean patents and applications for inventions since 1975

Electronic data base consulted during the international search (name of data base and, where practicable, search trerms used)
CAS ON LINE

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 92/14728 A (Korea Research Institute of Chemical Technology) 03 Sep. 1992. See the whole document	1-12
A	WO 96/12708 A (Korea Research Institute of Chemical Technology) 2 May 1996 See the whole document	1-12

☐ Further documents are listed in the continuation of Box C.

☐ See patent family annex.

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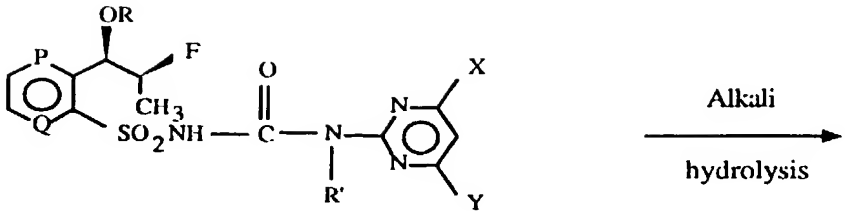
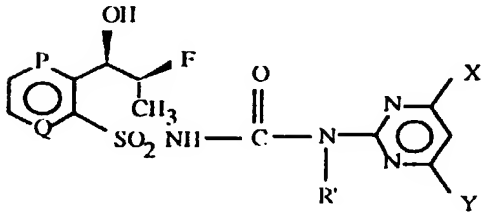
Date of the actual completion of the international search	Date of mailing of the international search report
05 JULY 2001 (05.07.2001)	10 JULY 2001 (10.07.2001)

Name and mailing address of the ISA/KR	Authorized officer
Korean Intellectual Property Office Government Complex-Daejeon, Dunsan-dong, Seo-gu, Daejeon Metropolitan City 302-701, Republic of Korea Facsimile No. 82-42-472-7140	CHO, Myung Sun Telephone No. 82-42-481-5605

Form PCT/ISA/210 (second sheet) (July 1998)



(I)'



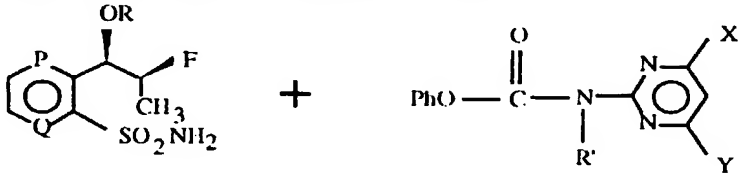
(I)"

wherein,

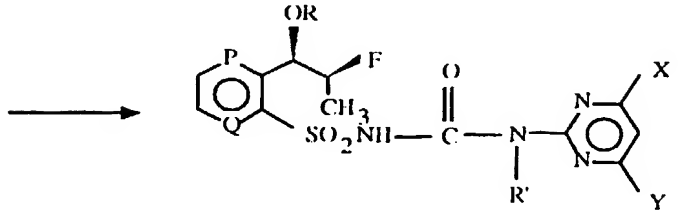
P, Q, R', X and Y are respectively defined as the above formula (I), and

R is defined as the above formula (I) except of hydrogen atom.

Also, the compounds of the above formula (I) according to the present invention can be prepared by reacting the erythro-type compound having the following formula (II) with the compound having the follwoing formula (III).



(II) (III)



(I)

wherein,

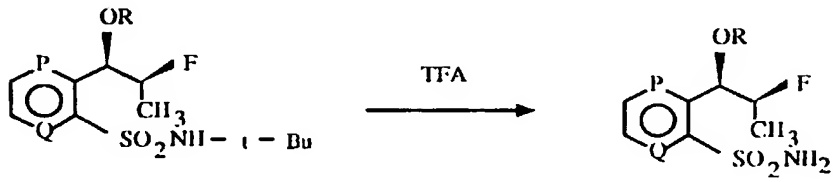
P, Q, R, R', X and Y are respectively defined as the above formula(I).

In the above reaction, unreacting solvent such as tetrahydrofuran, acetone, acetonitrile, dioxane, methylene chloride, toluene, butanone, pyridine, dimethylformamide, etc., may be used.

The reaction may be preferably carried out under strong base such as DBU or DABCO, etc. in a small quantity at the temperature of 20–80℃. The above reaction is referred to in U.S. patent No. 4,443,245 and thereafter the desired product can be obtained by acidifying by the method mentioned in European Patent No. 44,807. If necessery, a pure product can be obtained by purification by HPLC. Said, DBU represents 1,8 - diazabicyclo[5.4.0] undec-7-ene, and DABCO represents 1,4-diazabicyclo [2.2.2]octane.

Also, the compound of the formula(III) used for preparing the above formula(I) can be easily obtained by the prior art.

On the other hand, the erythro-type of the above formula(II) can be prepared by the following reaction scheme.



(IV) (II)

wherein,

P, Q and R are respectively defined as the above.

In the above reaction, the primary sulfonamide of erythro-type having the above formula(II) can be prepared by treating *N*-*t*-butylsulfonamide of the above formula(IV) with an acid such as trifluoroacetic acid (TFA) at the temperature of 0–50℃.

Also, the erythro-type of the above formula(IV) used in the above reaction can be

prepared by common acylation of the following formula(V). The pure erythro-type of the above formula(IV) can be seperated from mixture of threo- and erythro-type by purification such as column chromatograph, HPLC or prep-TLC.

The compound of the following formula(V) can be prepared by selective reduction of the compound of the following formula(VI) with selective reductant such as diisobutylaluminum hydride.

(VI) (V)

wherein,

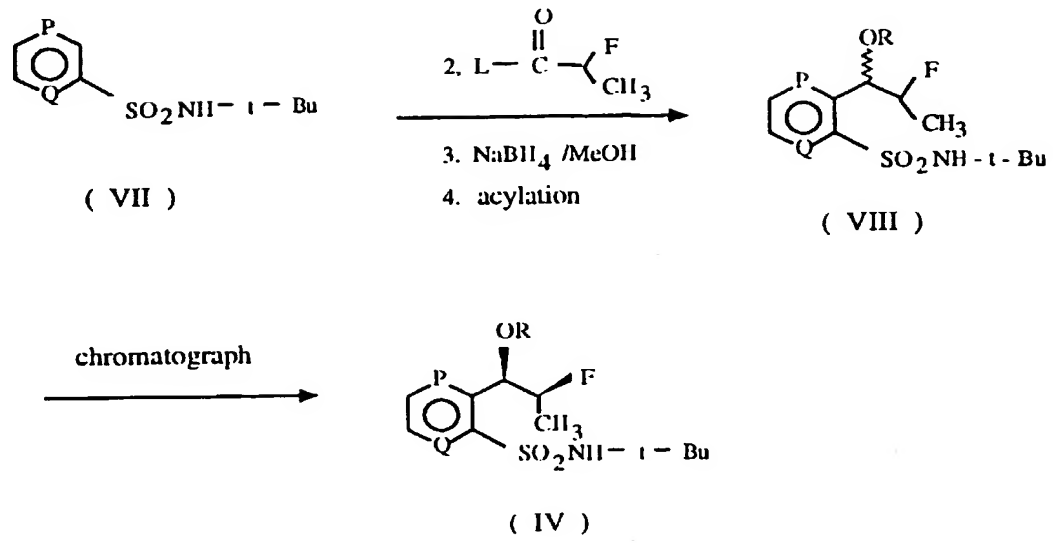
P and Q are respectively defined as the above.

DIBAL · H is diisobutylaluminum hydride.

In the above reaction, preferably P is N and Q is CH.

The pure erythro-type of the above formula(V) can be easily purified using column chromatograph.

The compound of the above formula(IV) can also be prepared by another process as shown in the following reaction.



(VII)

(VIII)

(IV)

wherein,

P and Q are respectively defined as the above formula(I),

R is defined as the above formula(I) except of hydrogen atom,

L is alkoxy, $N(CH_3)_2$ or $NCH_3(OCH_3)$, etc..

The above reaction process has been disclosed in Korea Patent Application No. 91-3704 and No. 91-3014. *n*-Butyl lithium of 2 equivalents are added in the compound of the above formula(VII) in THF solvent for 1~24 hours at -80 ~ + 30℃ to obtain dilithio salt, and then L-C(=O)-CHF-CH_3 is added at -70 ~ -80℃ to obtain ketone compound. Hydroxy compound is obtained by reduction of the ketone compound with $NaBH_4$, and then the compound of formula (VII) wherein R is acetyl group is obtained by acylation under acetic anhydride, DMAP and pyridine.

The pure erythro-type of the above formula (IV) can be easily obtained by separation and purification techniques such as HPLC, column chromatograph, prep-TLC, etc..

On the other hand, salts of the compound of the above formula(I) which are also useful as herbicide, can be prepared by various methods according to prior art. For example, metal salts of the compound can be prepared by reacting the above formula(I)

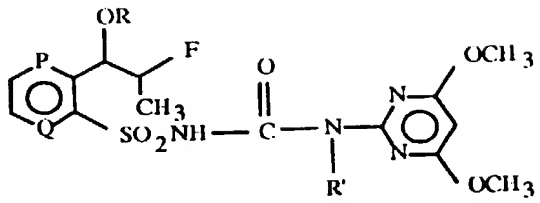
compound with strong basic anion, e.g. alkali or alkaline earth metal solution having hydroxyl group, alkoxide or carbonate, and also quaternary amine salt alike.

A salt of the formula(I) compound may also be obtained by cation exchange. The cation exchange can be carried out by directly reacting a solution containing cation for exchange with the solution of salt of formula(I), for example aqueous solution of alkali metal or quaternary amine salt. This method is useful when the desirable salt is water soluble, especially sodium, potassium or calcium salt.

The above manufacturing methods are summarized briefly, and the methods can be carried out easily by a person skilled in the technical field for manufacturing sulfonyl urea or organic composition.

The compounds of the above formula(I) according to the present invention may be specified as the following Table 1.

Table 1.



Isomer	P	Q	R	R'	m.p.(℃)
erythro	CH	CH	H	H	166 - 168
erythro	CH	CH	$\overset{O}{\overset{\|}{C}}CH_3$	H	191 - 193
erythro	N	CH	H	H	151 - 153
erythro	N	CH	$\overset{O}{\overset{\|}{C}}CH_3$	H	218 - 220
erythro	CH	N	H	H	
erythro	CH	N	$\overset{O}{\overset{\|}{C}}CH_3$	H	
erythro	CH	CH	$\overset{O}{\overset{\|}{C}}CH_2CH_3$	H	151-153
erythro	N	CH	$\overset{O}{\overset{\|}{C}}CH_2CH_3$	H	
erythro	CH	N	$\overset{O}{\overset{\|}{C}}CH_2CH_3$	H	

Isomer	P	Q	R	R'	m.p.(℃)
erythro	CH	CH	$\overset{O}{\overset{\|\|}{C}}CH_2CH_2CH_2$	H	
erythro	N	CH	$\overset{O}{\overset{\|\|}{C}}CH_2CH_2CH_2$	H	
erythro	CH	N	$\overset{O}{\overset{\|\|}{C}}CH_2CH_2CH_2$	H	
erythro	CH	CH	$\overset{O}{\overset{\|\|}{C}}OCH_3$	H	186 - 192
erythro	N	CH	$\overset{O}{\overset{\|\|}{C}}OCH_3$	H	
erythro	CH	N	$\overset{O}{\overset{\|\|}{C}}OCH_3$	H	
erythro	CH	CH	$\overset{O}{\overset{\|\|}{C}}OCH_2CH_3$	H	168 - 170
erythro	N	CH	$\overset{O}{\overset{\|\|}{C}}OCH_2CH_3$	H	
erythro	CH	N	$\overset{O}{\overset{\|\|}{C}}OCH_2CH_3$	H	
erythro	CH	CH	$\overset{O}{\overset{\|\|}{C}}OCH_2CH{=}CH_2$	H	

Isomer	P	Q	R	R'	m.p.(℃)
erythro	N	CH	$\overset{O}{\overset{\|\|}{C}}OCH_2CH=CH_2$	H	
erythro	CH	N	$\overset{O}{\overset{\|\|}{C}}OCH_2CH=CH_2$	H	
erythro	CH	CH	$\overset{O}{\overset{\|\|}{C}}OCH_2C\equiv CH$	H	
erythro	N	CH	$\overset{O}{\overset{\|\|}{C}}OCH_2C\equiv CH$	H	
erythro	CH	N	$\overset{O}{\overset{\|\|}{C}}OCH_2C\equiv CH$	H	
erythro	CH	CH	H	CH_3	139 - 140
erythro	CH	CH	$\overset{O}{\overset{\|\|}{C}}CH_3$	CH_3	162- 164
erythro	N	CH	H	CH_3	
erythro	N	CH	$\overset{O}{\overset{\|\|}{C}}CH_3$	CH_3	
erythro	CH	N	H	CH_3	
erythro	CH	N	$\overset{O}{\overset{\|\|}{C}}CH_3$	CH_3	

Isomer	P	Q	R	R'	m.p.(℃)
threo	CH	CH	H	H	189 - 191
threo	CH	CH	$\overset{O}{\overset{\|\|}{C}}CH_3$	H	194 - 196
threo	N	CH	H	H	173 - 175
threo	N	CH	$\overset{O}{\overset{\|\|}{C}}CH_3$	H	190 - 192
threo	CH	N	H	H	
threo	CH	N	$\overset{O}{\overset{\|\|}{C}}CH_3$	H	
threo	CH	CH	$\overset{O}{\overset{\|\|}{C}}CH_2CH_3$	H	
threo	N	CH	$\overset{O}{\overset{\|\|}{C}}CH_2CH_3$	H	
threo	CH	N	$\overset{O}{\overset{\|\|}{C}}CH_2CH_3$	H	
threo	CH	CH	$\overset{O}{\overset{\|\|}{C}}CH_2CH=CH_2$	H	
threo	N	CH	$\overset{O}{\overset{\|\|}{C}}CH_2CH=CH_2$	H	

Isomer	P	Q	R	R'	m.p.(℃)
threo	CH	N	$\overset{O}{\overset{\|\|}{C}}CH_2CH=CH_2$	H	
threo	CH	CH	$\overset{O}{\overset{\|\|}{C}}OCH_3$	H	
threo	N	CH	$\overset{O}{\overset{\|\|}{C}}OCH_3$	H	
threo	CH	N	$\overset{O}{\overset{\|\|}{C}}OCH_3$	H	
threo	CH	CH	$\overset{O}{\overset{\|\|}{C}}OCH_2CH_3$	H	
threo	N	CH	$\overset{O}{\overset{\|\|}{C}}OCH_2CH_3$	H	
threo	CH	N	$\overset{O}{\overset{\|\|}{C}}OCH_2CH_3$	H	
threo	CH	CH	$\overset{O}{\overset{\|\|}{C}}OCH_2CH=CH_2$	H	
threo	N	CH	$\overset{O}{\overset{\|\|}{C}}OCH_2CH=CH_2$	H	
threo	CH	N	$\overset{O}{\overset{\|\|}{C}}OCH_2CH=CH_2$	H	

Isomer	P	Q	R	R'	m.p.(℃)
threo	CH	CH	$\overset{O}{\overset{\|\|}{C}}OCH_2C{\equiv}CH$	H	
threo	N	CH	$\overset{O}{\overset{\|\|}{C}}OCH_2C{\equiv}CH$	H	
threo	CH	N	$\overset{O}{\overset{\|\|}{C}}OCH_2C{\equiv}CH$	H	
threo	CH	CH	H	CH_3	
threo	CH	CH	$\overset{O}{\overset{\|\|}{C}}CH_3$	CH_3	
threo	N	CH	H	CH_3	
threo	N	CH	$\overset{O}{\overset{\|\|}{C}}CH_3$	CH_3	
threo	CH	N	H	CH_3	
threo	CH	N	$\overset{O}{\overset{\|\|}{C}}CH_3$	CH_3	

The sulfonyl urea derivatives having erythro-type stereoisomer of the above formula(I) according to the present invention are useful as herbicides. The applied method is given below.

[Utility]

The compounds according to the present invention represent very high activity as pre- or post- emergence herbicides and water surface treatment or leaf treatment herbicides for rice.

The used amount of compound of the present invention is decided by several factor, that is, kinds of weeds, climate or weather, formulations selected, the applied method or the size of weed etc.

The active ingredients can be generally used from 1 g to 1 kg per hectare. Smaller quantity may be used in soil containing low organic matter or sandy soil, young plant or when the herbicidal effect is need of short-termed duration.

The compounds according to the present invention are especially effective as ingredient for control of weed in rice and wheat field, especially leaf-width weed, graminaceae weed and annual or perennial weed. The compounds are particularly effective for control of barnyard grass.

The list of weeds controllable by the compounds of the present invention is given below.

[the list of weeds]

<u>dicotyledon weeds genus:</u>

Sinapis, Lepidium, Galium, Stellaria, Matricaria, Anthemis, Galinsoga, Chenopodium, Urtica, Senecio, Amaranthus, Portulaca, Xanthium, Convolvulus, Ipomoea, Polygonum, Sesbania, Ambrosia, Cirsium, Carduus, Sonchus, Solanum, Rorippa, Rotala, Lindernia, Lamium, Veronica, Arbutilon, Emex, Datura, Viola, Galeopsis, Papaver, Centaurea.

<u>monocotyledon weeds genus:</u>

Echinochloa, Setaria, Panicum, Digitaria, Phleum, Poa, Festuca, Eleusine, Brachiaria, Lolium, Bromus, Avena, Cyperus, Sorghum, Agropyron, Cynodon, Monochoria, Fimbristylis, Sagittaria, Eleocharis, Scirpus, Paspalum, Dactyloctenium, Agrostis, Alopecurus, Apera, Heteranthera, Leptochloa.

The compounds of the present invention can be used as alone or in combination with two, three or four additives with other herbicides. The appropriate herbicides for mixed-using with the compounds of the present invention are given bleow. It is particularly useful for control of weeds to use the mixture of the compounds of the present invention and the below herbicides.

Common Name

acetochlor	acifluorfen
AC 252,214	AC 263,499
acrolein	alachlor
ametryn	amitrole
AMS	asulam
assure	atrazine
BAS-514	barban
benefin	bensulfuron methyl
bensulide	bentazon
benzofluor	benzoylprop
bifenox	bromacil
bromoxynil	butachlor
buthidazole	butralin
butylate	cacodylic acid
CDAA	CDEC
CGA 82725	CH-83
chloramben	chlorbromuron
chlorimuron ethyl	chloroxuron
chlorporpham	chlorsulfuron

chlortoluron	cinmethylin
clethodim	clomazone
cloproxydim	clopyralid
CMA	cyanazine
cycloate	cycluron
cyperquat	cyprazine
cyprazole	cypromid
dalapon	dazomet
DCPA	desmediphan
desmetryn	diallate
dicamba	dichlorbenil
dichlorprop	dichlofop
diethatyl	difenzoquat
dinitramine	dinoseb
diphenamid	dipropetryn
diquat	diuron
DNOC	DOWCO 453 ME
DPX-M6316	DSMA
endothall	EPTC
ethalfluralin	ethofumesate
express	fenac
fenoxapropethyl	fenuron
fenuron TCA	flamprop
fluazifop	fluazifopbutyl
fluazifop-P	fluchloralin
fluometuron	fluorochloridone
fluorodifen	fluoroglycofen
fluridone	fomesafen
fosamine	glyphosate

haloxyfop harmoney

hexaflurate hexazinone

HW-52 imazamethabenz

imazapyr imazaquin

imazethapyr ioxynil

isopropalin isoproturon

isouron isoxaben

karbutilate lactofen

lenacil linuron

MAA MAMA

MCPA MCPB

mecoprop mefluidide

methalpropalin methabenzthiazuron

metham methazole

methoxuron metolachlor

metribuzin metsulfuron methyl

MH molinate

monolinuron monuron

monuron TCA MSMA

My-93 napropamide

naproanilide naptalam

neburon nitralin

nitrofen nitrofluorfen

norea norflurazon

NTN-801 oryzalin

oxadiazon oxyfluorfen

paraquat pebulate

pendimethalin perfluidone

phenmedipham picloram

PPG-1013
procyazine
prometon
pronamide
propanil
propham
prynachlor
pyrazolate
quizalofop ethyl
secbumeton
siduron
SL-49
TCA
terbacil
terbuthylazine
terbutryn
thiobencarb
triclopyr
trifluralin
2,4-D
vernolate
xylachlor
KH-218
Pyrazoxyfen
CH-900
TSH-888
Dimepiperate
Phenobenzuron
Esprocab

pretilachlor
profluralin
prometryn
propachlor
propazine
prosulfalin
pyrazon
quizalofop
SC-2957
sethoxydim
simazine
sulfometuron methyl
tebuthiuron
terbuchlor
terbutol
thiameturon methyl
triallate
tridiphane
trimeturon
2,4-DB
X-52
Saturn
NSK-850
Dimension
Mefenacet
Dymron
Isoxapyrifos
JC-940
Methylbencab

Phenopylate	Benfuresate
S-275	Quinclorac
Londax	NC-311
TH-913	HW-52
DEH-112	SKH-301
Bromobutide	BAS517H
RE45601	RE36290
RO173664	HOE075032
ICIA6051	DPX-7881
MW801	CGA136872
DPXV9360	DPXE9636
SL950	ICIA02957
CGAI42464	MY15
MON7200	WL95481
DPXY6202	MON15100
SL160	ICIA0224
LS83556	BAS518H
CGA131036	DPXL5300
HOE70542	ICIA0604
ICIA0574	LS846215

[Formulation]

Formulations for the use of the compounds of formula(I) can be prepared in conventional ways. They include dusts, granules, pellets, solutions, suspensions, emulsions, wettable powders, emulsifiable concentrates and the like. Many of these may be applied directly.

Sprayable formulations can be prepared in suitable media and used at spray volumes of from a few liters to several houndred liters per hectare. High strength compositions are primarily used as intermediates for further formulation. The

formulations, broadly, contain about 0.1% to 98.9% by weight of active ingredient(s) and at least one of (1) about 0.1% to 20% surfactant(s) and (2) about 1% to 99.8% solid or liquid inert diluent(s) are recommended. More specially, the formulations will contain these ingredients in the following approximate proportions:

Table 2.

Formulations	Weight Percent(%)		
	Active Ingredient	Diluent	Surface Active Agent
Wettable Powders	20-90	1-74	1-10
Oil Suspension, Emulsions, Solution Emulsifiable Concentrates	3-50	40-95	0.1-15
Aqueous Suspension	10-50	40-84	1-20
Dusts	1-25	70-98.9	0.1-5
Granules and Pellets	0.1-95	5-99.8	0.1-15
High strength Composition	90-98.9	1-10	0.1-2

Lower or higher levels of active ingredient can, of course, be present depending on the intended use and the physical properties of the compound. Higher ratios of surface active agent to active ingredient are sometimes desirable, and are achieved by incorporation into the formulation or by tank mixing.

Typical solid diluents are mentioned in the writings of Watkins, et al.("Handbook of Insecticide Dust Diluents and Carrier" 2nd Ed., Dorland Books, Caldwell, N.J.,) and other solid diluents can be used.

The more absorptive diluents are preferred for wettable powders and the denser ones for dusts.

Typical liquid diluents and solvents are mentioned in the writings of Marsden ("Solvents Guide", 2nd Ed., Interscience, New York, 1950).

Solubility under 0.1% is preferred for concentrated suspension; concentrated

solution is preferably stable against phase separation at 0℃.

The surface active agents and their using method is mentioned in the writings of McCutcheon (McCutcheon's Detergents and Emulsifiers Annual, Mc Publishing Corp., Ridgewood, N. J.,) and Sisely et al. (Sisely snd Wood, "Encyclopedia of Surface Active Agents", Chemical Publishing Co., Inc., New York, 1964).

All the above formulations may contain a small amount of additives to reduce foaming, caking, corrosion and the growth of microorganisms.

The preparation methods of such compositions are well known. A solution can be made only by blending properties and a fine solid composition by blending and pulverizing.

Suspension agents can be made by wet milling method (U.S. Patent No. 3,060,084) and granules and pellets can be made by spraying the active ingredient on preformed granular carrier, or by Agglomeration method (J.E. Browing, "Agglomeration " Chemical Engineering, Dec. 4,1967, pp147 / "Perry's Chemical Engineer's Handbook," 5th Ed., Mcgraw-Hill, New York, 1973, pp 8-57ff).

For further information regarding the art of formulations, see for example: US patent No. 3,235,361 / 3,309,192 / 2,891,855, G. C. Klingman, "Weed Control as a Science", John Wiley and Sons, Inc., New York, 1961, pp.81-96 / J. D. Fryer and S. A. Evans, "Weed Control Handbook", 5th Ed., Blackwell Scientific Publications Oxford, 1968, pp.101-103.

The compounds of the present invention can be used independently and may be used in combination with any other commercial herbicides. To specify some more the manufacturing and using of the compounds of the present invention, the detailed examples are described below.

EXAMPLE 1

Erythro 2-(1-acetoxy-2-fluoro-*n*-propyl)-*N*-*t*-butyl-benzenesulfonamide.

Erythro *N*-*t*-butyl-2-(2-fluoro-1-hydroxy-*n*-propyl)-benzenesulfonamide (3.5 g) was dissolved in 50 *ml* of methylene chloride and herein acetic anhydride (1.25 *ml*),

pyridine(1.1 *ml*) and *N,N*-dimethyl aminopyridine(0.12 g) were added. After stirring for 1 hour, the reacting solution was diluted with methylene chloride and washed with 5% hydrochloric acid solution. The seperated organic layer was dried with magnesium sulfate, filtered and concentrated. And then the obtained residue was chromatographed through silicagel using 1 : 3(v/v) solution of ethyl acetate/hexane to afford 3.7 g of the desired product(white solid).

m.p. : 134 ~ 135 ℃

^{1}H NMR(200MHz, $CDCl_3$) : δ 1.25(s, 9H), 1.36(dd, 3H, J_{H-H}=6.4Hz, J_{H-F}= 25.3Hz),2.17(s, 3H), 4.86-5.22(m, 1H), 5.47(brs, 1H), 6.68(dd, 1H, J_{H-H}=3Hz, J_{H-F}=18.6Hz), 7.41-7.71(m, 3H), 8.04-8.12(m, 1H).

IR(KBr) ν (C=O) 1715 cm^{-1}

Crystal data of product prepared by the above EXAMPLE 1 is the following.

Crystal data

Molecular Formula	:	$C_{15}H_{22}FNO_4S$
Measured Density(D_m)	:	1.3 Mgm^{-3}
Molecular Weight(M_r)	:	331.4
Used Wave Length(λ)	:	0.71069 Å
Crystal System	:	monoclinic system

No. of diffraction data used in measuring lattic constant : 25

Size of unit cell

a = 13.693(6) Å

b = 14.731(15) Å

c = 8.737(5) Å

β = 106.51(5) Å

Volume of unit cell (V)	:	1690(1) Å
Independent Molecularity(Z)	:	4
Calculating Density(Dx)	:	1.303 Mg m^{-3}

Hygroscopic Coefficient(μ)	:	1.74 mm^{-1}
Experimental temperature	:	299 K
Size of crystal used in measuring	:	0.3 x 0.2 x 0.2 mm
Color	:	Colorless
Crystal source	:	obtained on synthesizing

Data Collection

Used Diffractometer	:	CAD-4 diffractometer made in Netherland Enraf-Nonius company
Maximum angle of Scan	:	$\theta_{max} = 24°$
Scanning Method	:	$\omega / 2\theta$ scans
Range of Miller Index	:	h=-15→15 k=0→16 l=0→9
Absorption Correction Method	:	did not correct.
measuring method	:	3 of standard data were confirmed every time diffraction data was measured.
Change of standard data on measuring	:	no change
No. of Measured Data	:	2549
No. of Independent Data	:	2549
No. of measured data in significant having threefold of standard deviation	:	2337 [F>3σ(F)]

Refinement

Data used in refining	:	F
Refined parameter	:	
non-hydrogen atom	:	atomic coordinates x,y,z and anisotropic temperature factor (u_{ij})
hydrogen atom	:	isotropic temperature factor (u)
hydrogen atom coupled nitrogen[H(N)]	:	atomic coordinates x,y,z and isotropic temperature factor (u)
No. of parameter refined by the minimum square method	:	224
Final Reliancity factor(R)	:	0.0598

Sequencity of refining process variables by the minimum square method (S)

: 3.5233

Manimum differential-composite electron density(△Pmax) : 0.481 e Å^{-3}

Minimum differential-composite electron density(△Pmin) : 0.349 e Å^{-3}

No. of data used in refining : 2337 [F>30(F)]

Atomic scattering factor used in X-ray crystalography is described in the Table 3 and stereoconfiguration of innermolecular atoms are given in Figure 1.

Table 3.

Atoms	x	y	z	Ueq
S	0.2176(1)	0.3425(0)	0.7251(1)	0.040
F	0.0756(2)	0.6606(1)	0.8577(3)	0.083
O(1)	0.2426(2)	0.6366(1)	0.7567(3)	0.052
O(2)	0.3216(2)	0.5628(2)	0.6045(4)	0.083
O(3)	0.2209(2)	0.2488(1)	0.7683(3)	0.058
O(4)	0.1302(1)	0.3754(1)	0.6074(2)	0.051
N	0.3128(2)	0.3635(2)	0.6569(3)	0.045
C(1)	0.2312(2)	0.4071(2)	0.9026(3)	0.039
C(2)	0.2183(2)	0.5022(2)	0.9026(3)	0.037
C(3)	0.2415(2)	0.5461(2)	1.0485(4))	0.052
C(4)	0.2731(3)	0.4985(3)	1.1913(4)	0.061
C(5)	0.2813(3)	0.4053(3)	1.1882(4)	0.061
C(6)	0.2616(2)	0.3593(2)	1.0443(4)	0.053
C(7)	0.1759(2)	0.5586(0)	0.7527(4)	0.043
C(8)	0.0707(2)	0.5970(2)	0.7359(4)	0.052
C(9)	-0.0067(3)	0.5269(3)	0.7416(5)	0.066
C(10)	0.3137(3)	0.6290(2)	0.6793(4)	0.050
C(11)	0.3779(3)	0.7120(3)	0.6955(5)	0.070
C(12)	0.4207(2)	0.3314(2)	0.7215(4)	0.057
C(13)	0.4770(3)	0.3671(4)	0.6105(5)	0.097
C(14)	0.4689(4)	0.3677(7)	0.8839(6)	0.162
C(15)	0.4217(5)	0.2279(4)	0.787(12)	0.191

EXAMPLE 2

Threo 2-(1-acetoxy-2-fluoro-*n*-propyl)-*N*-*t*-butyl-benzenesulfonamide

From threo *N*-*t*-butyl-2-(2-fluoro-1-hydroxy-*n*-propyl)-benzenesulfonamide (6 g) was obtained 6.4 g of the desired product (white solid) using the same method of EXAMPLE 1.

m.p. : 126 ~ 127 ℃

^{1}H NMR(200MHz, $CDCl_3$) : δ 1.23(s, 9H), 1.36(dd, 3H, J_{H-H}=6.4Hz, J_{H-F}=23.6Hz), 2.18(s, 3H), 4.73-5.11(m, 1H), 5.54(brs, 1H), 6.49(dd, 1H, J_{H-H}=3.8Hz, J_{H-F}=21.6Hz), 7.41-7.69(m, 3H), 8.02-8.11(m, 1H).

IR(KBr) ν (C=O) 1715 cm^{-1}

EXAMPLE 3

Erythro 2-(1-acetoxy-2-fluoro-*n*-propyl)-benzenesulfonamide

Erythro 2-(1-acetoxy-2-fluoro-*n*-propyl)-*N*-*t*-butyl-benzenesulfonamide (3.7 g) was dissolved in trifluoroacetic acid(20 *ml*) after stirring for 24 hours at room temperature was concentrated under vacuum and residue solution was diluted with methylene chloride and washed with 5% $NaHCO_3$ solution.

The organic layer was dried with magnesium sulfate, filtered and concentrated. and then the concentrated solution was column chromatograped using eluate of ethyl acetate/hexane to afford 2.3 g of the desired product (white solid).

m.p. : 105 ~ 107 ℃

^{1}H NMR(200MHz, $CDCl_3$) : δ 1.33(dd, 3H, J_{H-H}=6.4Hz, J_{H-F}=24.6Hz), 2.18(s, 3H), 4.85-5.23(m, 1H), 5.55(brs, 2H), 6.53-6.68(m, 1H), 7.46-7.75(m, 3H), 8.06-8.13(m, 1H).

EXAMPLE 4

Threo 2-(1-acetoxy-2-fluoro-*n*-propyl)-benzenesulfonamide

The desired product 3.9 g(white solid) was obtained by the same method of EXAMPLE 3 from threo 2-(1-acetoxy-2-fluoro-*n*-propyl)-*N*-*t*-butyl-benzenesulfonamide

(6.4 g).

m.p. : 126 ~ 128 ℃

^{1}H NMR(200MHz, $CDCl_3$) : δ 1.36(dd, 3H, J_{H-H}=6.4Hz, J_{H-F}=24.2Hz), 2.18(s, 3H), 4.75-5.12(m, 1H), 5.57(brs, 2H), 6.38-6.53(m, 1H), 7.46-7.66(m, 3H), 8.06-8.13(m, 1H).

EXAMPLE 5

Erythro 2-(1-acetoxy-2-fluoro-*n*-propyl)-*N*-[(4,6-dimethoxypyrimidin-2-yl)-aminocarbonyl]-benzenesulfonamide [Compound No. 4]

Erythro 2-(1-acetoxy-2-fluoro-*n*-propyl)-benzenesulfonamide (2.3 g) was dissolved in 20 *ml* of acetonitrile and herein 2.3 g of phenyl (4,6-dimethoxy pyrimidin-2-yl) carbamate was added at room temperature. 1 *ml* of DBU was slowly added dropwised . The reacting solution was stirred for 30 minutes and diluted with 100 *ml* of methylen chloride. Washed with 50 *ml* of 5% hydrochloric acid solution and 50 *ml* of water, the organic layer was dried with magnesium sulfate, filtered and concentrated. The obtained residue was treated with ethyl acetate/hexane/ethylether to afford 2.9 g of the desired product (white solid).

m.p. : 191 ~ 193 ℃

^{1}H NMR(200MHz, $CDCl_3$) : δ 1.33(dd, 3H, J_{H-H}=6.4Hz, J_{H-F}=24.6Hz), 2.04(s, 3H), 3.96(s, 6H), 4.86-5.25(m, 1H), 5.80(s, 1H), 6.70-6.82(m, 1H), 7.18-7.70(m, 4H), 8.30-8.40(m, 1H), 13.15(brs, 1H).

EXAMPLE 6

Threo 2-(1-acetoxy-2-fluoro-*n*-propyl)-*N*-[(4,6-dimethoxypyrimidin-2-yl)amino-carbonyl]-benzenesulfonamide [Compound No. 5]

5.3 g of the desired product was obtained using the same method of EXAMPLE 5 from 3.9 g of threo 2-(1-acetoxy-2-fluoro-*n*-propyl)-benzenesulfonamide.

m.p. : 194 ~ 196 ℃

^{1}H NMR(200MHz, $CDCl_3$) : δ 1.33(dd, 3H, J_{H-H}=6.4Hz, J_{H-F}=24.2Hz), 2.04(s, 3H), 3.96(s, 6H), 4.80-5.14(m, 1H),

5.80(s, 1H), 6.42-6.62(m, 1H), 7.23-7.70(m, 4H),
8.27-8.37(m, 1H), 12.95(brs, 1H).

EXAMPLE 7

Erythro *N*-[(4,6-dimethoxypyrimidin-2-yl)aminocarbonyl]-2-(2-fluoro-1-hydroxy- *n*-propyl)-benzenesulfonamide [Compound No. 1]

Erythro 2-(1-acetoxy-2-fluoro-*n*-propyl)-*N*-[(4,6-dimethoxypyrimidin-2-yl)amino-carbonyl]-benzenesulfonamide (2.9 g) was dissolved in 60 *ml* of tetrahydrofuran and herein 0.9 g of lithium hydroxide and 10 *ml* of water were added. After stirring for 12 hours at room temperature, acidified with hydrochloric acid at 0 ℃. The reacting solution was diluted with 100 *ml* of ethyl acetate and once washed with water. The organic layer was dried with magnesium sulfate, filtered and concentrated. The obtained residue was treated with ethyl ether and hexane to efford 2.3 g of the desired product. (white solid)

m.p. : 166 ~ 168 ℃

^{1}H NMR(200MHz, $CDCl_3$) : δ 1.33(dd, 3H, $J_{H\text{-}H}$=6.4Hz, $J_{H\text{-}F}$=24.6Hz),
3.08(brs, 1H), 3.96(s, 6H), 4.86-5.25(m, 1H),
5.80(s, 1H), 5.89-6.07(m, 1H), 7.36-8.24(m, 5H),
12.82(brs, 1H).

IR(KBr) ν (C=O) 1705 cm^{-1}

EXAMPLE 8

Threo *N*-[(4,6-dimethoxypyrimidin-2-yl)aminocarbony)]-2-(2-fluoro-1-hydroxy-*n*-propyl]-benzenesulfonamide [Compound No. 2]

3.0g of the desired product (white solid) was obtained using the same method of EXAMPLE 7 from threo 2-(1-acetoxy-2-fluoro-*n*-propyl)-*N*-[(4,6-dimethoxypyrimidin-2-yl)aminocarbonyl]-benzenesulfonamide(3.7 g).

m.p. : 189 ~ 191 ℃

^{1}H NMR(200MHz, $CDCl_3$) : δ 1.36(dd, 3H, $J_{H\text{-}H}$=6.4Hz, $J_{H\text{-}F}$=24.2Hz),
3.0(brs, 1H), 3.96(s, 6H), 4.78-5.11(m, 1H),
5.80(s, 1H), 5.79-5.91(m, 1H), 7.22-7.78(m, 4H),

8.13-8.22(m, 1H), 12.75(brs, 1H).

IR(KBr) ν (C=O) 1691 cm^{-1}

EXAMPLE 9

Erythro 2-(1-acetoxy-2-fluoro-*n*-propyl)-3-pyridinesulfonamide.

5.0 g of erythro 2-(1-acetoxy-2-fluoro-*n*-propyl)-*N*-(1,1-dimethylethyl)-3-pyridinesulfonamide was dissolved in 20 *ml* of trifluoroacetic acid. After stirring for 12 hours at 35 ℃, the reaction solution was concentrated under vacuum. The residue was dissolved in methylene chloride and washed with $NaHCO_3$ solution. The organic layer was dried with anhydrous magnesium sulfate and the residue was crystallized with ethyl acetate and hexane to afford 3.0 g of the desired product.

m.p. : 141 ~ 143 ℃

^{1}H NMR(200MHz, $CDCl_3$) : δ 1.55(dd, 3H, J_{H-H}=6.5Hz, J_{H-F}=25Hz),
2.18(s, 3H), 4.93-5.29(m, 1H), 5.68(brs, 2H),
6.55-6.62(m, 1H), 7.43-7.50(m, 1H),
8.35-8.38(m, 1H), 8.82-8.85(m, 1H)

Crystal data of the product prepared by the above EXAMPLE 9 is the following.

Crystal Data

Molecular Formula	:	$C_{10}H_{13}FN_2O_4S$
Crystal System	:	Trichlinic system
Space Group	:	P1
Molecularity of inner unit lattice(Z)	:	2
a = 8.529, b =10.270, c = 8.528, α =110.09, β = 99.28,γ =110.08		
No. of independent diffraction data	:	1953
Final Reliancity factor	:	6.19%
X-ray Wave Length	:	1.5405

Atomic scattering factor used to X-ray crystalography is described in the following Table 4 and stereoconfiguration of innermolecular atoms are given in Figure 2.

Table 4.

Atoms	x	y	z	Ueq
S	0.63350(0)	0.56940(0)	0.37580(1)	0.205(4)
F	0.9981(5)	0.9201(5)	0.7942(7)	0.29(1)
N	0.4564(8)	0.5644(8)	0.2715(8)	0.27(2)
O1	0.6198(6))	0.9893(5)	0.7386(6)	0.23(1)
O2	0.3911(7)	0.8254(7)	0.4979(8)	0.28(1)
O3	0.7802(7)	0.6911(6)	0.3769(7)	0.28(1)
O4	0.6179(7)	0.4174(6)	0.3044(7)	0.27(1)
C1	0.6273(8))	0.6136(7)	0.5963(8)	0.19(1)
C2	0.6479(8)	0.7545(8)	0.7121(8)	0.19(1)
N3	0.6190(8)	0.7774(7)	0.8588(7)	0.22(1)
C4	0.573(1)	0.6565(8)	0.9094(9)	0.28(2)
C5	0.561(1)	0.5174(9)	0.807(1)	0.27(2)
C6	0.5858(9)	0.4914(8)	0.6428(9)	0.23(2)
C7	0.7158(8)	0.9012(7)	0.8863(9)	0.21(1)
C8	0.9037(9)	1.0076(8)	0.8095(8)	0.21(2)
C9	0.994(1)	1.1395(9)	0.768(1)	0.28(2)
C10	0.4606(9)	0.9429(8)	0.6262(9)	0.24(2)
C11	0.388(1)	1.056(1)	0.689(1)	0.40(3)
HA	0.4615	0.6782	0.3215	0.0740
HB	0.3448	0.4873	0.2893	0.3006
H4	0.5438	0.6717	1.0313	0.0542
H5	0.5324	0.4277	0.8508	0.0636
H6	0.5733	0.3807	0.5557	0.0222
H7	0.7043	0.8652	0.5485	0.0480
H8	0.8978	1.0570	0.9413	0.0785
H9A	0.9217	1.2086	0.7800	0.4316
H9B	0.9996	1.0959	0.6356	0.0814
H9C	1.1261	1.2090	0.8595	0.0846
H11A	0.2604	1.0164	0.5974	0.1528
H11B	0.4757	1.1654	0.6998	0.2462
H11C	0.3748	1.0680	0.8169	0.4053

EXAMPLE 10

Threo 2-(1-acetoxy-2-fluoro-*n*-propyl)-3-pyridinesulfonamide

1.6 g of the desired product was obtained using the same method of EXAMPLE 9 from threo 2-(1-acetoxy-2-fluoro-*n*-propyl)-*N*-(1,1-dimethylethyl)-3-pyridinesulfonamide (3.0 g)

m.p. : 164 ~ 165 ℃

^{1}H NMR(200MHz, $CDCl_3$) : δ 1.17(dd, 3H, J_{H-H}=6.5Hz, J_{H-F}=23.9Hz), 2.16(s, 3H), 5.03-5.38(m, 1H), 5.79(brs, 2H), 6.54-6.64(m, 1H), 7.43-7.49(m, 1H), 8.35-8.40(m, 1H), 8.80-8.83(m, 1H)

EXAMPLE 11

Erythro 2-(1-acetoxy-2-fluoro-*n*-propyl)-*N*-[(4,6-dimethoxypyrimidin-2-yl) aminocarbonyl]-3-pyridinesulfonamide [Compound No. 10]

5.1 g of the desired product (white solid) was obtained using the same method of EXAMPLE 5 from 3.9 g of erythro 2-(1-acetoxy-2-fluoro-*n*-propyl-3-pyridinesulfonamide.

m.p. : 218 ~ 220 ℃

^{1}H NMR(200MHz, $CDCl_3$) : δ 1.46(dd, 3H, J_{H-H}=6.4Hz, J_{H-F}=24.9Hz), 2.04(s, 3H), 3.96(s, 6H), 4.98-5.26(m, 1H), 5.78(s, 1H), 6.55-6.62(m, 1H), 7.2(brs, 1H), 7.45-7.51(m, 1H), 8.60-8.65(m, 1H), 8.80-8.83(m, 1H), 13.23(br s, 1H)

EXAMPLE 12

Threo 2-(1-acetoxy-2-fluoro-*n*-propyl)-*N*-[(4,6-dimethoxypyrimidin-2-yl) aminocarbonyl]-3-pyridinesulfonamide [Compound No. 11]

2.9 g of the desired product (white solid) was obtained using the same method of EXAMPLE 5 from 2.3 g of threo 2-(1-acetoxy-2-fluoro-*n*-propyl)-3-pyridinesulfonamide.

m.p. : 190 ~ 192 ℃

^{1}H NMR(200MHz, $CDCl_3$) : δ 1.28(dd, 3H, J_{H-H}=6.4Hz, J_{H-F}=23.9Hz),
2.01(s, 3H), 3.97(s, 6H), 5.08-5.38(m, 1H),
5.79(s, 1H), 6.49-6.60(m, 1H), 7.20(brs, 1H),
7.46-7.53(m, 1H), 8.64-8.69(m, 1H),
8.82-8.85(m, 1H), 13.08(brs, 1H)

EXAMPLE 13

Erythro *N*-[(4,6-dimethoxypyrimidin-2-yl)aminocarbonyl]-2-(2-fluoro-1-hydroxy- *n*-propyl)-3-pyridinesulfonamide [Compound No. 7]

2.1 g of the desired product (white solid) was obtained using the same method of EXAMPLE 7 from 3.0 g of erythro 2-(1-acetoxy-2-fluoro-*n*-propyl)-*N*-[(4,6-dimethoxypyrimidin-2-yl)aminocarbonyl]-3-pyridinesulfonamide

m.p. : 151 ~ 153 ℃

^{1}H NMR(200MHz, $CDCl_3$) : δ 1.37(dd, 3H, J_{H-H}=6.2Hz, J_{H-F}=24.8Hz),
3.95(s, 6H), 4.11(d, 1H), 4.66-4.95(m, 1H),
5.57-5.69(m, 1H), 5.78(s, 1H), 7.33(brs, 1H),
7.46-7.53(m, 1H), 8.62-8.67(m, 1H),
8.79-8.82(m, 1H), 12.98(brs, 1H)

EXAMPLE 14

Threo *N*-[(4,6-dimethoxypyrimidi n-2-yl)aminocarbonyl]-2-(2-fluoro-1-hydroxy- *n*-propyl)-3-pyridinesulfonamide.[Compound No. 8]

0.7 g of the desired product (white solid) was obtained using the same method of EXAMPLE 7 from 1.0g of threo 2-(1-acetoxy-2-fluoro-*n*-propyl)-*N*-[(4,6-dimethoxy-pyrimidin-2-yl)aminocarbonyl]-3-pyridine sulfonamide.

m.p. : 173 ~ 175 ℃

^{1}H NMR(200MHz, $CDCl_3$) : δ 1.48(dd, 3H, J_{H-H}=6.3Hz, J_{H-F}=24.2Hz),
3.97(s, 6H), 4.40(d, 1H), 4.90-5.30(m, 1H),
5.31-5.55(m, 1H), 5.82(s, 1H), 7.3(brs, 1H),
7.49-7.55(m, 1H), 8.58-8.63(m, 1H),
8.82-8.85(m, 1H), 13.0(brs, 1H)

EXAMPLE 15

The herbicidal effect of the compounds of the present invention was tested by the greenhouse test, the method is as followings.

Pre-emergence test

To produce a suitable preparation of active compound, 1 part by weight of active compound was mixed with 5 parts by weight of acetone, 1 part by weight of alkylaryl polyglycol ether as emulsifier was added and the solution diluted with water to the desired concentration. Seeds of the test plants are shown in normal soil and, after 24 hours, watered with the preparation of the active compound.

It is expedient to keep constant the amount of water per unit area. The concentrat ion of the active compound in the preparation is of no importance, only the amount of active compound applied per unit area being decisive. After three weeks, the degree of damage to the plants was rated in % damage in comparison to the development of the untreated control.

The figures denote :

0% = no action (like untreated control)

20% = slight effect

70% = herbicidal effect

100% = total destruction.

In this test, the active compounds(I) according to the preparation examples exhibited a better herbicidal activity against mono- and dicotyledon weeds.

EXAMPLE 16

post-emergence test

To produce a suitable preparation of active compound, 1 part by weight of active compound was mixed with 5 parts by weight of acetone, 1 part by weight of emulsifier was added and the solution diluted with water to the desired concentration.

Test plants which had a height of 5～15 ㎝ were sprayed with the preparation of the active compound in such a way as to apply the particular amounts of active compound desired per unit area. The concentration of the spray liquid was so chosen that the particular amounts of active compound desired were applied in 2,000 *l* of water / ha. After three weeks, the degree of damage to the plants was rated in % damage in comparision to the development of the untreated control.

The figures denote :

0% = no action(like untreated control)

20% = slight effect

70% = herbicidal effect

100% = total destruction.

In this test, the active compounds(I) according to the preparation examples exhibited a better herbicidal activity against mono- and dicotyledon weeds.

EXAMPLE 17

Fresh-water treatment paddy submerged test

A plastic pot having a surface area of 60㎠ or 140㎠ was filled with a small amount of fertilizer, after then, the sterilized paddy soil of puddled state at the depth of 5-㎝.

Seeds of barnyard grass, umbrella plant, dayflower, monochoria, toothcup, smartweed, and bulrush et al. and perennial nutrition body of flat-sedge and arrowhead et al., were seeded or planted in surface layer of soil, and pregerminated rice with 2-3 leaves was transplanted one root per pot at the depth of 2㎝.

After planting, the pot was watered for a day at the depth of 2㎝ and the manufactured herbicide was spot-treated on the plant in manner sililar to the field condition (4mg/pot).

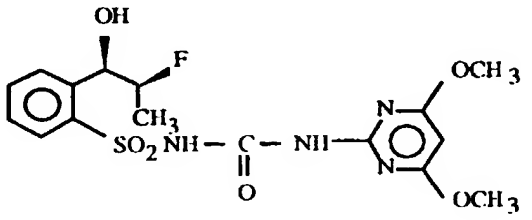
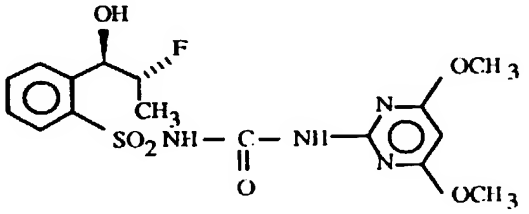
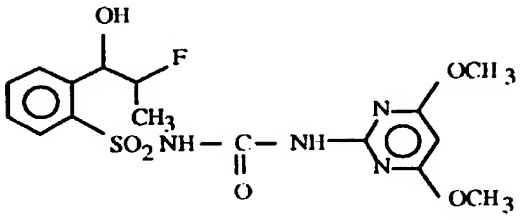
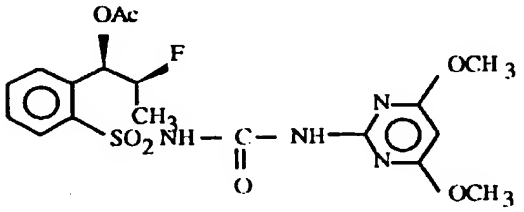
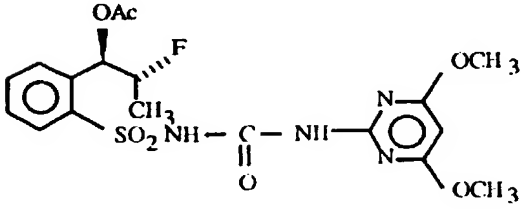
Two weeks after treatment, herbicidal effect was measured by the same survey standard as that for field condition.

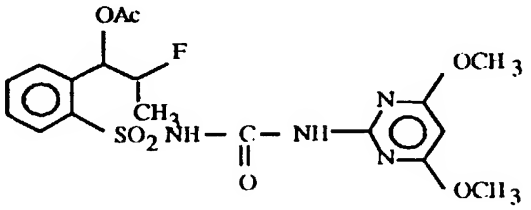
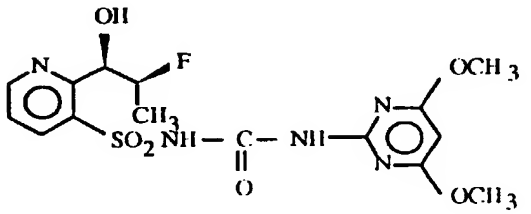
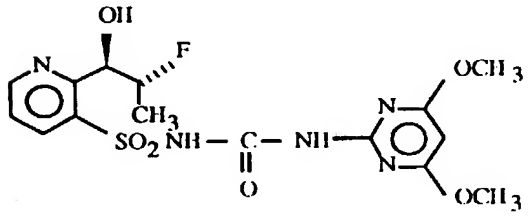
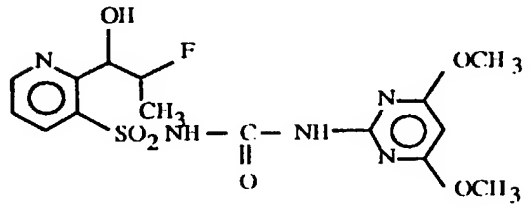
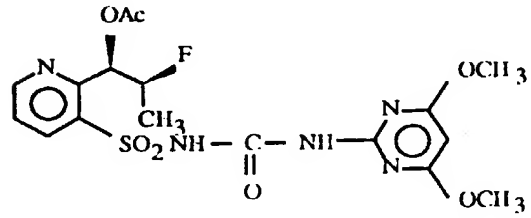
It is understood that the above examples are illustrative but not limitative of the present invention and that other embodiments within the spirit and scope of the invention

will suggest themselves to those skilled in the art.

The following Table 5 represents the formula of active ingredients of the present invention. The following Table 6~8 represents pre- and post-emergence herbicidal effect of active ingredients.

Table 5.

Structures		Compound No.
	erythro	1
	threo	2
	mixture	3
	erythro	4
	threo	5

Structures		Compound No.
	threo	6
	erythro	7
	threo	8
	mixture	9
	erythro	10

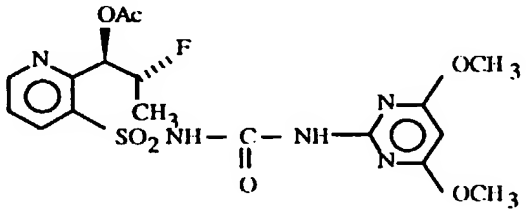
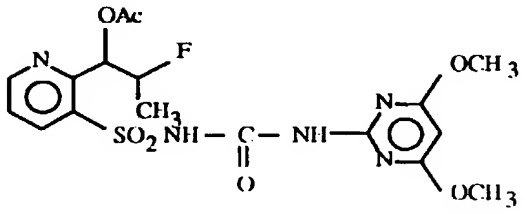
Structures		Compound No.
	threo	11
	mixture	12

Table 6. PRIMARY SCREENING (PADDY SUBMERGED)-Herbicide

Compound No.	DAT*	kg/ha	ECHOR[1]	SCPJU[2]	MOOVA[3]	CYPSE[4]	SAGPY[5]
1	2	0.0125	100	100	100	100	100
2	2	0.0125	70	70	100	100	100
3	2	0.0125	95	80	80	100	60
4	3	0.0125	95	90	100	85	100
5	3	0.0125	70	80	70	50	95
6	2	0.0125	85	80	80	60	75
7	2	0.0125	100	100	100	100	100
8	2	0.0125	20	0	40	90	90
9	2	0.0125	60	40	40	90	100
10	2	0.0125	100	95	100	100	100
11	2	0.0125	20	0	50	90	50
12	2	0.0125	80	30	0	100	100

(note) *DAT : Day After Treatment

(1)ECHOR : Bchinochloa crus-galli P.BEAUV. var. oryzicolo OHWI. : Barnyard grass

(2)SCPJU : Scirpus juncoides ROXB. : Bulrush

(3) CYPSE : Cyperus serotinus ROTTB. : Flat-sedge

(4) MOOVA : Monochoria vaginalis PRESL. : Monochoria

(5) SAGPY : Sagittaria pygmaea MIQ. : Arrow head

Table 7. Harmful Effects Test of Herbicides*1

DAT	g/ha	Harmful Effects of Herbicides	
		Compound No.1	Compound No.7
5	5	0	0
5	10	10	0
5	20	20	0

*1 transplanted rice : 5 DAT treatment after transplanting of 2 leaves rice

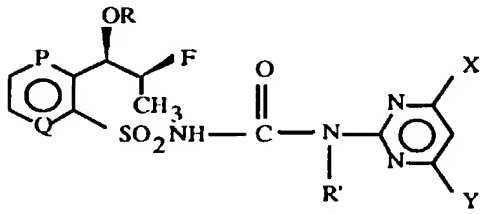
survey : Comparison of living body weight after herbicidal treatment

Table 8. Percentage Control for Barnyard grass

Leaf Stage	g/ha	Percentage Control(%)	
		Compound No.1	Compound No.7
1 Leaf	2.5	86	88
(6DAS)	5	95	95
	10	95	95

WHAT IS CLAMED IS :

1. Sulfonyl urea derivatives of the following formula(I) having substituent of erythro-type stereoisomer,



(I)

wherein,

P and Q, as equivalent or different group respectively, are CH or N, and present as aromatic ring including P and Q as benzene or pyridine ring ;

R is H, $R^a-\overset{O}{\overset{\|}{C}}-$ or $R^a-X^a-\overset{O}{\overset{\|}{C}}-$ group, wherein R^a is C_1~C_4 alkyl, C_1~C_3 haloalkyl, C_2 ~C_4 alkenyl or C_2 ~C_4 alkynyl group, wherein X^a is O, S, NH or NR^a group;

R' is H or CH_3 group; and

X and Y are independently halogen atom, C_1~C_2 alkyl, C_1~C_2 alkoxy or C_1~C_2 haloalkoxy group.

2. Sulfonyl urea derivatives according to claim 1, wherein said R is hydrogen atom or acetyl group, said P and Q are independently CH or N, and said X and Y are respectively methoxy group.

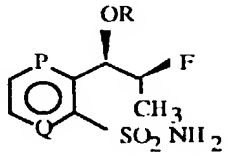
3. Sulfonyl urea derivative according to claim 1, wherein said formula(I) is erythro *N*-[(4,6-dimethoxy-pyrimidin-2-yl)aminocarbonyl]-2-(2-fluoro-1-hydroxy-*n*-propyl)-benzenesulfonamide.

4. Sulfonyl urea derivatives according to claim 1, wherein said formula(I) is erythro 2-(1-acetoxy-2-fluoro-*n*-propyl)-*N*-[(4,6-dimethoxy-pyrimidin-2-yl)-aminocarbonyl]-benzenesulfonamide.

5. Sulfonyl urea derivatives according to claim 1, wherein said formula(I) is erythro *N*-[(4,6-dimethoxy-pyrimidin-2-yl)aminocarbonyl]-2-(2-fluoro-1- hydroxy-*n*-propyl)-3-pyridinesulfonamide.

6. Sulfonyl urea derivatives according to claim 1, wherein said formula(I) is erythro 2-(1-acetoxy-2-fluoro-*n*-propyl)-*N*-[(4,6-dimethoxy-pyrimidin-2-yl)aminocarbonyl]-3-pyridinesulfonamide.

7. Intermediate compounds of the following formula(II) having erythro-type,



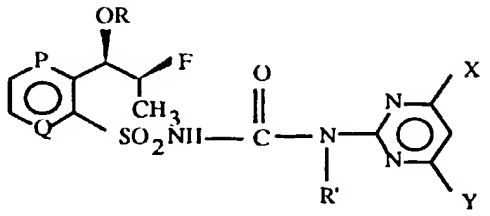
(II)

wherein, R,P and Q is respectively as defined in the above claim 1.

8. Intermediate compound according to claim 7, wherein said formula(II) is erythro 2-(1-acetoxy-2-fluoro-*n*-propyl)-benzenesulfonamide.

9. Intermediate compound according to claim 7, wherein said formula(II) is erythro 2-(1-acetoxy-2-fluoro-*n*-propyl)-3-pyridinesulfonamide.

10. Herbicidal compositions including sulfonyl urea derivatives of following formula (I) as an effective component.



(I)

wherein P, Q, R, R', X and Y are respectively as defined in the above claim 1.

11. Herbicidal composition according to claim 10, wherein said sulfonyl urea derivatives of formula(I) is that R is hydrogen atom or acetyl group; Q is CH; P is CH or N; R' is hydrogen atom; and X and Y are respectively methoxy group.

12. Herbicidal composition according to claim 10, wherein said sulfonyl urea derivatives of formula(I) is erythro *N*-[(4,6-dimethoxy-pyrimidine-2-yl)-aminocarbonyl]-2-(1-hydroxy-2-fluoro-*n*-propyl)-benzenesulfonamide.

13. Herbicidal composition according to claim 10, wherein said sulfonyl urea derivatives of following formula(I) is erythro *N*-[(4,6-dimethoxy-pyrimidin-2-yl)aminocarbonyl]-2-(1-hydroxy-2-fluoro-*n*-propyl)-3-pyridine-sulfonamide.

FIG. 1

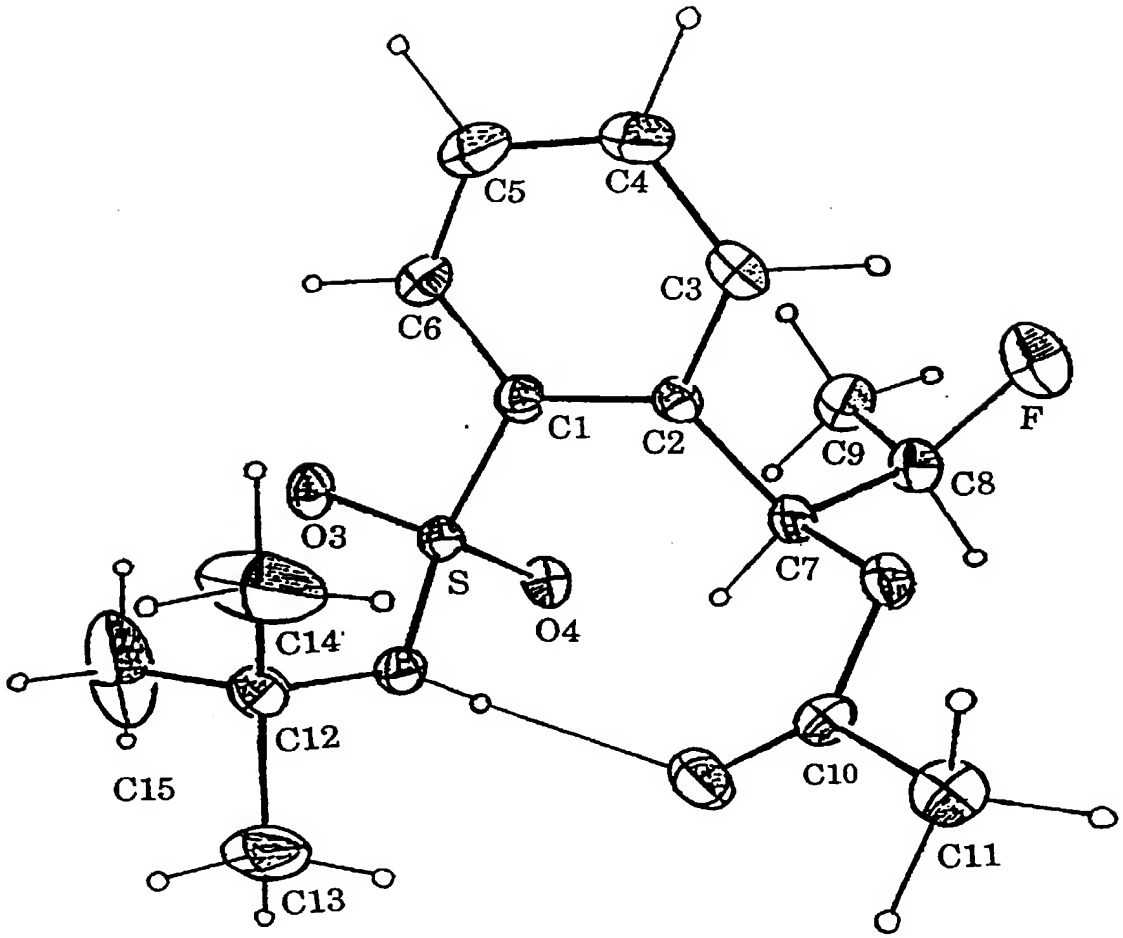
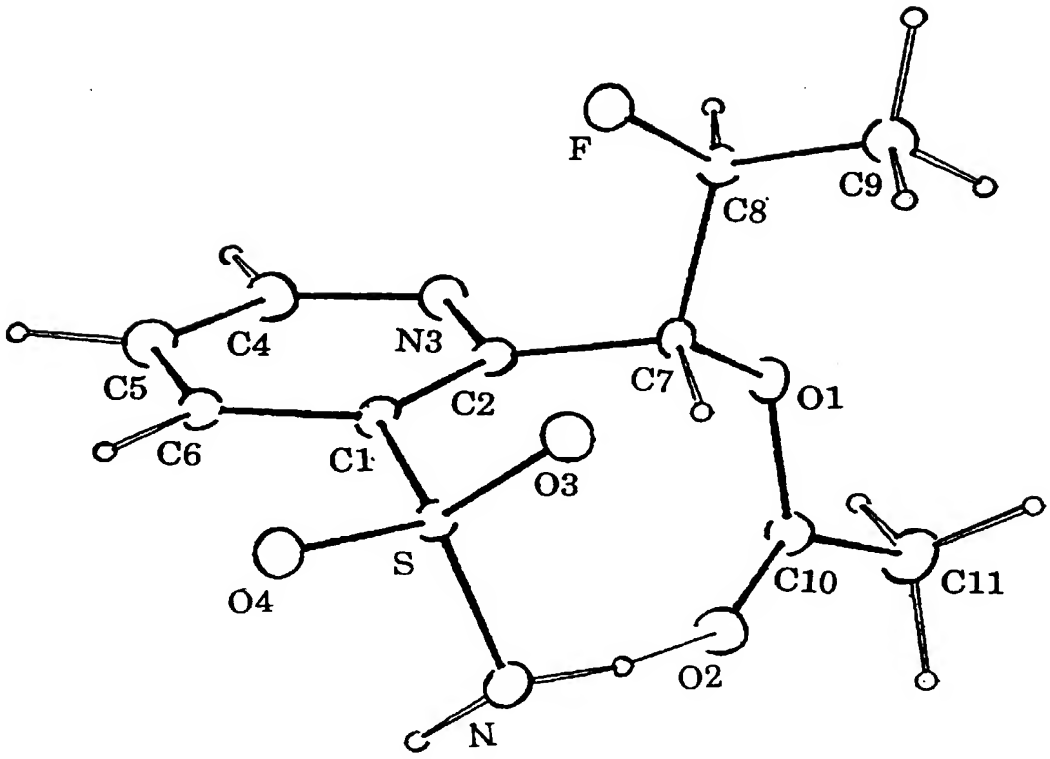


FIG. 2



INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR 94/00147

A. CLASSIFICATION OF SUBJECT MATTER

IPC[6]: C 07 D 239/42,401/14,213/73; C 07 C 311/29; A 01 N 47/36

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC[6]: C 07 D 239/42,401/14,213/73; C 07 C 311/29; A 01 N 47/36

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 044 807 A2 (CIBA-GEIGY AG) 27 January 1982 (27.01.82), claims 1,27,29; (cited in the application).	1,7,10
A	US 4 443 245 A (MEYER et al.) 17 April 1984 (17.04.84), abstract; (cited in the application).	1,10
A	EP 0 240 216 A1 (SUMITOMO CHEMICAL COMPANY) 07 October 1987 (07.10.87), page 3, lines 31-33.	1,10
A	US 4 532 328 A (KLESCHICK) 30 July 1985 (30.07.85), column 1, lines 12-15.	1,10
A	EP 0 512 953 A1 (CIBA-GEIGY AG) 11 November 1992 (11.11.92), abstract.	7,8

☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* Special categories of cited documents:

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
04 August 1995 (04.08.95)	14 August 1995 (14.08.95)

Name and mailing address of the ISA/ AT	Authorized officer:
AUSTRIAN PATENT OFFICE Kohlmarkt 8-10 A-1014 Vienna	Lux e.h.
Facsimile No. 1/53424/535	Telephone No. 1/5337058/31

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/KR 94/00147

Im Recherchenbericht angeführtes Patentdokument Patent document cited in search report Document de brevet cité dans le rapport de recherche	Datum der Veröffentlichung Publication date Date de publication	Mitglied(er) der Patentfamilie Patent family member(s) Membre(s) de la famille de brevets	Datum der Veröffentlichung Publication date Date de publication
EP A2 44807	27-01-82	AT E 4526	15-09-83
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		BG B2 60335	27-05-94
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		BR A 8104619	06-04-82
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		DE C0 3172974	02-01-86
		DE C0 3173493	27-02-86
		DK A 3186/81	18-01-82
		DK A 1441/90	13-06-90
		DK A0 1441/90	13-06-90
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		DK B 163664	23-03-92
		DK C 163664	17-08-92
		DK B 164901	07-09-92
		DK B 165182	19-10-92
		DK C 164901	18-01-93
		DK B 166082	08-03-93
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		DK C 166082	02-08-93
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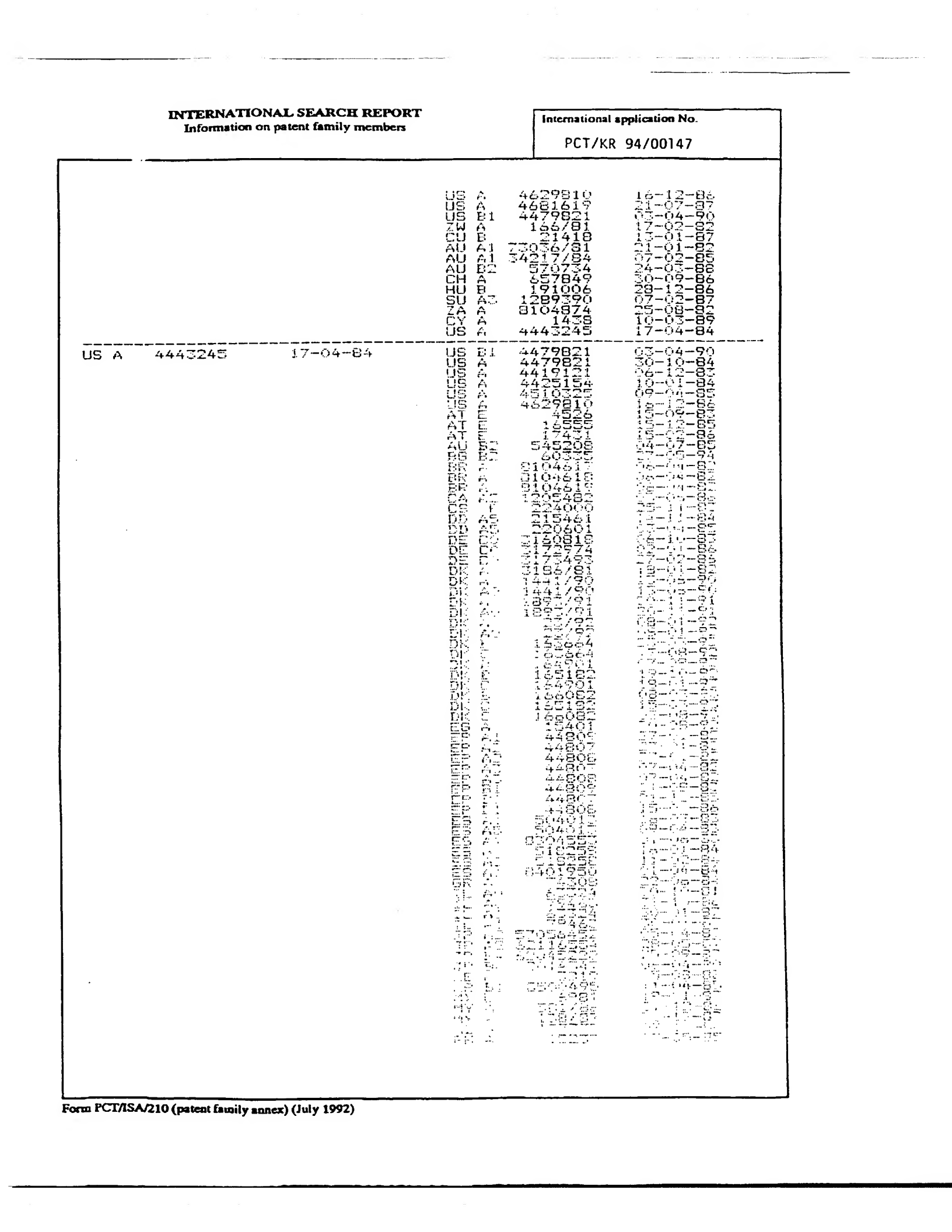

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